

Research Paper

Removal of carbamazepine from MBR effluent by electrochemical oxidation (EO) using a Ti/Ta₂O₅-SnO₂ electrodeKhum Gurung^{a,*}, Mohamed Chaker Ncibi^a, Marina Shestakova^a, Mika Sillanpää^{a,b}^a Laboratory of Green Chemistry, School of Engineering Science, Lappeenranta University of Technology, Sammonkatu 12, FI-50130, Mikkeli, Finland^b Department of Civil and Environmental Engineering, Florida International University, Miami, FL, 33174, USA

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ABSTRACT

This study aims at investigating the electrochemical oxidation (EO) of carbamazepine (CBZ) synthetic solutions and real membrane bioreactor (MBR) effluent using newly developed Ti/Ta₂O₅-SnO₂ electrodes to enhance CBZ removal. The characterization of the prepared Ti/Ta₂O₅-SnO₂ electrodes was performed by using scanning electron microscope, energy dispersive X-ray spectroscope, atomic force microscope, and cyclic voltammetry analyses. The main operating parameters influencing the CBZ removal efficiency in synthetic solutions using Ti/Ta₂O₅-SnO₂ electrodes were evaluated including the applied current density, initial CBZ concentration, pH, and temperature. The optimum removal of CBZ (20 mg L^{-1}) and TOC reached 75.5%, and 71.1%, respectively, after 8 h of electrolysis, under current density of 9 mA cm^{-2} , pH 6, temperature of 30 °C, and using 0.1 M Na₂SO₄ as supporting electrolyte. Increasing current density and temperature influenced the CBZ removal, unlike pH which did not have significant influence on CBZ removal. The performance of Ti/Ta₂O₅-SnO₂ electrode was compared with conventional Ti/PbO₂ electrode in terms of CBZ removal efficiencies and stability of the electrodes. The results showed that under the same operating conditions, the CBZ removal efficiency of Ti/PbO₂ electrode was slightly higher than of Ti/Ta₂O₅-SnO₂ (77.9 and 71.7%, respectively). Nonetheless, the use of this newly developed electrode is more energy-efficient as it required the lowest energy consumption of 60.3 kWh m^{-3} to achieve optimum CBZ removal, in addition to fact that no heavy metals were leached (unlike the PbO₂ electrode). Furthermore, a complete degradative removal of real MBR effluents spiked with CBZ was achieved when electrolyzed under the optimized conditions of CBZ synthetic solutions. Overall, the EO based on the use of Ti/Ta₂O₅-SnO₂ electrode was found to be a reliable approach to remove CBZ from contaminated waters, with promising potential for integration with MBR technology to remediate CBZ.

1. Introduction

Pharmaceutically active compounds (PhACs) have gained a great deal of attention among researchers in recent years as emerging micropollutants with long-term potential threats to aquatic environment and human health [1–4]. These PhACs are introduced to aquatic ecosystems primarily from the effluents of wastewater treatment plants (WWTPs). In addition, direct and unsafe discharge of untreated wastewaters from agriculture, industries and hospitals are also reported to contribute to the release of PhACs into the aquatic ecosystems [2,3,5–7].

Carbamazepine, which is used for the treatment of epilepsy, depression, trigeminal neuralgia and wide variety of mental disorders, is one of the frequently identified PhAC in various aquatic environments [2,3,7]. The world-wide annual consumption of CBZ is more than 1000 tons and about 28% of it ends up in WWTPs as unmetabolized forms.

[3,5]. In Finland, the annual consumption of CBZ is around 3.3 tons, with comparatively more concentrations in winter seasons than in summer at WWTP effluents [8]. CBZ is highly recalcitrant to biodegradation in conventional activated sludge processes and photo-degradation (more than 100 days) [2]. In fact, many researchers have documented difficulties in removing CBZ, with biodegradation removal of only less than 10% [3,4,6,8]. Thus, it is crucial to apply highly efficient degradation technologies for the removal of CBZ in order to achieve the highest mineralization or generate non (or less) toxic intermediates.

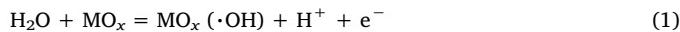
In this context, MBRs have been studied for the removal of various PhACs including CBZ by many researchers [9–11]. However, a relatively low removal (0–28%) of CBZ was reported in MBR processes when treating synthetic and real wastewaters [2,9,11]. Thus, biodegradation and membrane filtration alone are not efficient enough for the removal of CBZ. Therefore, in order to meet the future legislations

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regarding the stringent limits of PhACs from WWTP effluents, MBR process integrated with various advanced oxidation processes (AOPs) has gained increasing interest.

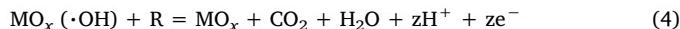
AOPs are oxidation-based technologies applied in aqueous phase in order to deconstruct organic pollutants via the in-situ generated highly reactive oxygen species, mainly hydroxyl radicals ($\cdot\text{OH}$) [12]. They are promising and environmentally friendly methods for the treatment of wastewaters contaminated with a wide range of recalcitrant PhACs. Among the various AOPs, EO processes are of growing interest for water and wastewater decontamination due to their low cost and high efficiency [3]. In EO processes, dissolved organic pollutants are mainly oxidized by (i) direct anodic oxidation on the anode surface by charge transfer, and (ii) reaction with physio and/or chemisorbed hydroxyl radical ($\cdot\text{OH}$) generated from water oxidation (Eq. (1)) [13,14]. Hydroxyl radicals are extremely reactive oxidants (2.8 V (vs. SHE)) with the life time of less than a second, which makes their detection very challenging [15]. The subsequent oxidation mechanism of organic compounds depends on the behavior of anodes, which are divided as “non-active” and “active” [13–16]. In both cases, firstly, water molecules splitted and leading to the formation of OH at the anode oxide surface (MO_x) (Eq. (1))[17].



At ‘active’ anodes, OH radicals are chemisorbed (strongly adsorbed), thus allow only selective oxidation of organics (R), which involves intermediate step of higher oxide formation (Eqs. (2) and (3))[14,16].



On the other hand, at ‘non-active’ anodes, the formation of higher oxide is excluded and OH radicals are physisorbed without interaction on the anode surface [14,16]. Moreover, ‘non-active’ anodes with high O₂-overpotential towards water oxidation allow good electrochemical stability and can generate many strong (OH) radicals predominantly leading to the complete combustion of organics (Eq. (4)) [15–17].



The major problems of EO process are the polarization and passivation of electrodes, related either to the poor mass transfer, corrosive environment, formation of polymer films or the inevitable formation of oxide interlayers due to the considerable porosity in supported catalyst films, [14,15,18]. In any cases, those phenomena result in the attenuation of the efficiency and service life of electrodes.

Various anodes such as PbO₂, and more recently, boron-doped diamond (BDD) have shown an interesting electro-degradation efficiency for CBZ [2,3,6]. Nevertheless, the higher cost of BDD electrodes and the possible leaching of lead (Pb) from PbO₂ coated electrodes tend to compromise their applicability in large-scale applications [19,20]. In fact, PbO₂ is one of the widely studied anode on the electrochemical degradation of PhACs [2,6,21,22]. PbO₂ anodes are inexpensive, relatively easy to prepare, has low electrical resistivity, and has a large surface area [23]. In this context, Ti/Ta₂O₅-SnO₂ (SnO₂ semi-conductor doped with Ta₂O₅) are eco-friendly electrodes, which were proven to be efficient in the oxidation of some organic compounds [18,24].

The main aim of the current research is to evaluate the efficiency of this novel electrode to remove persistent CBZ drug from synthetic solutions and the real MBR effluent. First, the EO of synthetic solution loaded with CBZ was investigated by monitoring and optimizing the major influencing factors including current density, pH, and temperature, under various initial concentrations of CBZ. In addition, the degradation efficiency and stability of Ti/Ta₂O₅-SnO₂ were compared with Ti/PbO₂ electrodes. Furthermore, optimized operating conditions in EO process were applied for the treatment of real MBR effluent spiked with CBZ. This study is the first research work on the EO of CBZ using novel Ti/Ta₂O₅-SnO₂ electrodes in synthetic solutions and real

wastewaters.

2. Materials and methods

2.1. Reagents and materials

All the reagents and materials used were of analytical grade. CBZ (meets USP testing specifications), Titanium foil (99.7% trace metal basis, 2 mm thick), SnCl₂·2H₂O ($\geq 99.99\%$ trace metal basis), TaCl₅ ($\geq 99.99\%$ trace metal basis), NaOH ($\geq 98\%$ anhydrous), H₃PO₄ (85%), Na₂SO₄ ($\geq 99\%$ anhydrous) were purchased from Sigma-Aldrich, USA. Commercial Ti/PbO₂ electrodes (5 cm × 10 cm × 2 mm) were supplied by Magneto, Netherlands.

A synthetic stock solution containing CBZ (20 mg L⁻¹) was prepared using Milli-Q water (18.2 MΩ·cm), stirred at 500 rpm for 24 h at room temperature [5]. Then, 0.1 M (14.2 mg L⁻¹) of Na₂SO₄ (better supporting electrolyte than NaCl regarding economical, effectiveness and environmental aspects) was added to increase conductivity of the solution. In this regard, the possible formation of organic chlorine by-products is also limiting the use of NaCl in electrochemical processes [5]. Finally, the synthetic stock solution was stored in the refrigerator at 4 °C for further use.

2.2. Preparation of Ti/Ta₂O₅-SnO₂ electrodes

Ti/Ta₂O₅-SnO₂ electrodes were prepared by thermal decomposition of precursor solutions on Ti substrates [25]. For the preparation of the electrodes, the methodology is detailed in a previous study conducted in our laboratory [26]. The optimized nominal composition of Ta (7.5 at.%) and Sn (92.5 at.%) were used to prepare precursor solutions by dissolving SnCl₂·2H₂O and TaCl₅ salts in absolute alcohol (pro analysis, Panreac), where total concentration of metal ions was kept constant (0.04 M). At first, Ti substrate plates (5 cm × 10 cm × 2 mm) were pre-treated by mechanical polishing and followed by degreasing in 10 wt.% NaOH for 10 min and etching in boiled 18 wt.% HCl (pro analysis, Fluka) for 30 min, and finally rinsed carefully using Milli-Q water. Secondly, the precursor solution was applied over only one side of the pre-treated Ti substrates by drop casting method. The precursor solution of 1 mL volume was dropped on to the Ti substrate, uniformly distributed using the tip of a Pasteur glass pipette, dried in oven at 80 °C for 5 min, and then annealed in muffle furnace at 550 °C for 5 min. The process was repeated until 8 layers of ultrathin film deposition of the precursor solution, which attributed highest electro-catalytic properties of the electrodes [26]. After the final layer, electrodes were additionally annealed at 550 °C for 10 h to enhance the formation of composite oxides of Ta and Sn on the electrode surface via thermal decomposition. The final composite oxides on Ti substrate gave the wide band gap n-type SnO₂ semi-conductor extrinsically doped with Ta₂O₅. After 10 h, electrodes were cooled down and kept in an ultrasonic bath for 5 min in order to remove the surface impurities and deformations, and then oven dried at 105 °C. Thus, the precursor material deposited only one side of Ti substrates had surface area of 50 cm² and the deposited material was equal to 1.10 mg cm⁻² ± 5%.

2.3. Physicochemical and electrochemical characterization of the electrodes

Microstructure of the Ti/Ta₂O₅-SnO₂ electrodes was analyzed by using scanning electron microscope (SEM) (Hitachi, SU3500, Japan) using 5 kV of acceleration voltage. The chemical analysis of selected areas of the electrode surface was performed with energy-dispersive X-ray spectroscope (UltraDry™ Compact EDS Detector, Thermo Fisher, USA). The AFM images were taken by using atomic force microscope (AFM) (NX10, Park, Korea) using the non-contact mode.

The electrochemical characterization of the Ti/Ta₂O₅-SnO₂ electrode was performed by conducting cyclic voltammetry (CV) measurements using an Autolab (PGSTAT 12 Potentiostat/Galvanostat,

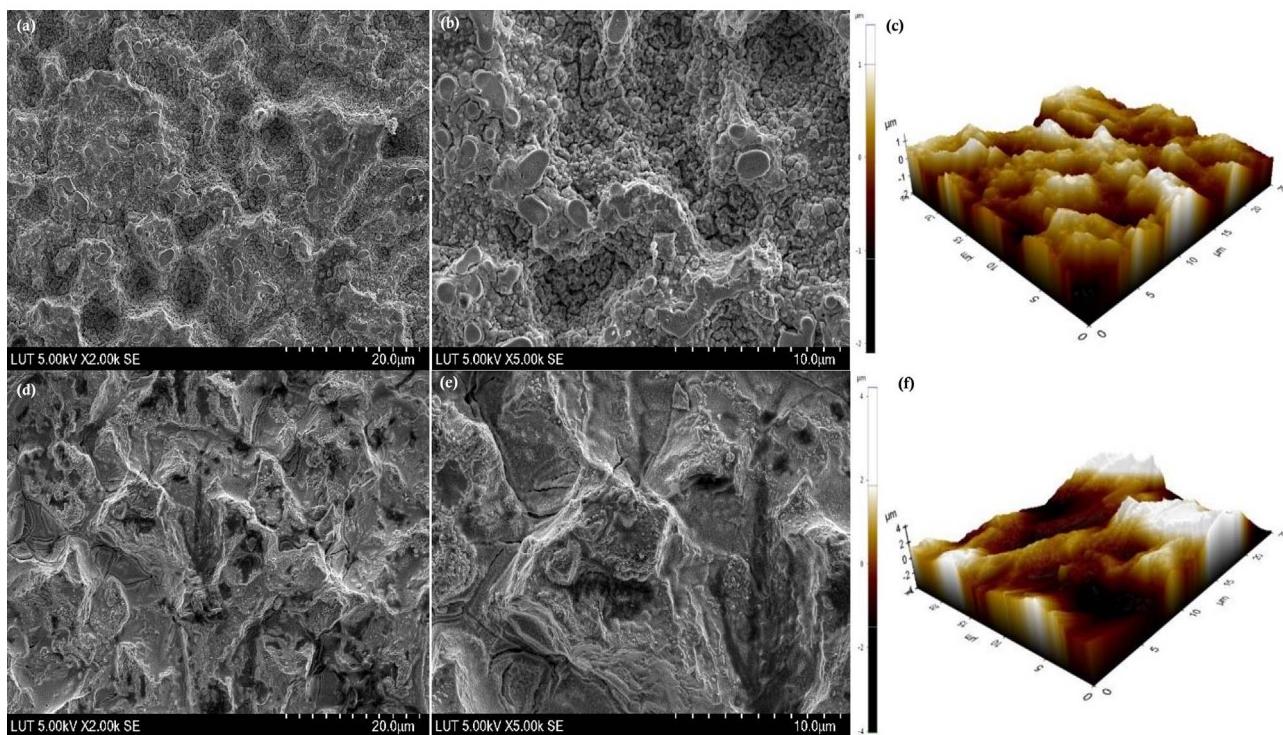


Fig. 1. SEM and AFM images of $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ electrodes before electrolysis (a–c) and after 8 h of electrolysis (d–f) under current density of 9 mA cm^{-2} .

Metrohm, Switzerland) connected with GPES software (Eco Chemie, Netherlands). All the CV measurements were performed in a three electrode cell (100 mL). A coiled platinum wire was used as counter electrode and saturated calomel electrode (SCE) as reference electrode, whereas $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ electrode ($1 \text{ cm} \times 1 \text{ cm}$) was used as working electrode. First, the voltammograms were recorded at different scan rates from 20 to 100 mV s^{-1} in 0.1 M Na_2SO_4 aqueous solution between 0.6 and 0.8 V (vs. SCE), where only double-layer currents (non-faradic) were observed for estimating the relative roughness factor. Second, the voltammograms were plotted between the anodic currents against electrical voltage between 0.2–2.5 V (vs. SCE) at scan rate of 100 mV s^{-1} with or without CBZ in 0.1 M Na_2SO_4 aqueous solution. In each of the assays, aqueous solution inside the CV cell was deoxygenated by argon bubbling prior to the measurements.

2.4. Electrochemical degradation assays

The experimental set-up for the electrochemical degradation system is shown in Fig. S1. The CBZ-containing solutions were electrolyzed using an open glass reactor of 500 mL capacity with cooling jacket for the circulation of thermostated water, under a 500 rpm stirring. The reaction temperature was maintained at $11 \pm 1^\circ\text{C}$. The electrochemical unit consisted of $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ electrode as anode and pure Ti plate (same area) as cathode, with an inter-electrode gap of 10 mm. The electrical power was applied via DC power supply (EX752M-Multimode PSU, TTI, UK) with maximum current and potential rating of 4A and 150 V, respectively. All the electrochemical degradation assays were performed under galvanostatic conditions. Each experiment was run for 8 h with sampling every hour.

2.5. Analytical methods

2.5.1. CBZ measurements

The removal of CBZ was analyzed by UV-vis spectrophotometer (Lambda 45, Perkin Elmer, USA) by measuring the absorbance of UV light by CBZ at 210 nm. A calibration curve was created by scanning different concentrations of CBZ from 1 to 30 mg L^{-1} (Fig. S1,

Supplementary data) in order to calculate the residual CBZ concentration and thus the removal efficiency. As for the real MBR effluent, since the spiked samples have low concentration of CBZ ($10 \mu\text{g L}^{-1}$), they were analyzed with LC-MS/MS (Acquity UPLC/Xevo TQMS, USA) using 5 cm C18 column (Acquity UPLC BEH, USA).

2.5.2. Other measurements

Non-Purgeable Organic Carbon (NPOC) was measured with TOC-analyzer (TOC-V Series-CPN, Shimadzu, Japan) to evaluate the mineralization efficiency. The pH was measured using pH meter (pH 110, VWR). The electrical conductivity was monitored by using conductivity meter (Euroscan Con 6, EUTECH, USA).

The energy consumption (EC) needed for the electrochemical treatment per volume of working solution was calculated based on Eq. (5) [15].

$$\text{EC (kWh m}^{-3}\text{)} = \frac{\text{U}_{\text{cell}} \text{It}}{\text{V}_s} \quad (5)$$

where U_{cell} is the average potential difference of the cell (in V), I is the applied current (in A), t is the electrolysis time (in h), and V_s is the working solution volume (in dm^3).

3. Results and discussion

3.1. Microstructural characterization

SEM and AFM micrographs of $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ electrode before and after the 8 h of electrolysis using the current density of 9 mA cm^{-2} are shown in Fig. 1a-f. In SEM images, the electrode surface before electrolysis (Fig. 1a-b) showed foam-like porous microstructure with large numbers of relatively homogenous agglomerates mainly related to the density of Ta_2O_5 crystals, which can partially increase the surface roughness. In fact, the porosity and relative surface roughness depend on the active oxide layers. When the electrode was subjected to electrolysis for 8 h, the surface exhibited structural changes in the surface showing heterogeneously-distributed porous network and more rough structure as shown in Fig. 1d–e.

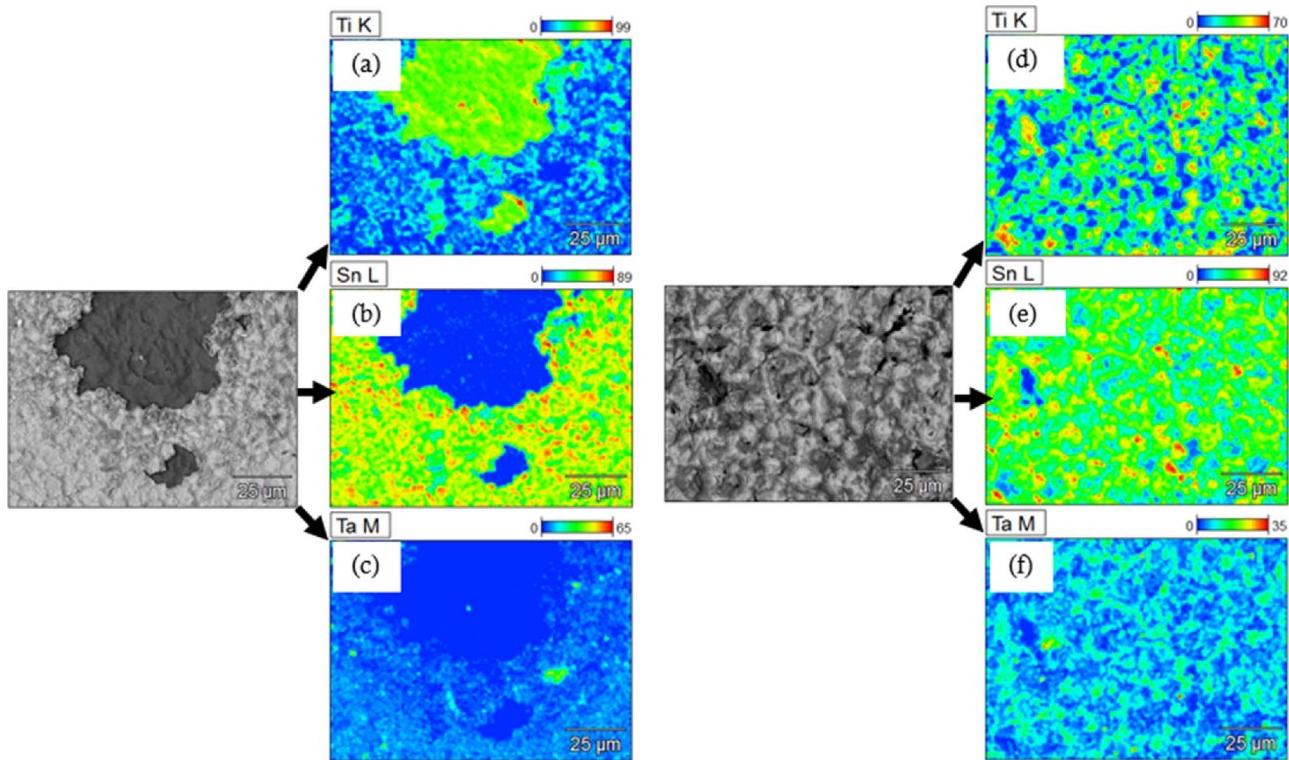


Fig. 2. EDX mappings of $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ electrodes before (a–c) and after 8 h of electrolysis (d–f) under current density of 9 mA cm^{-2} .

Likewise, the AFM analysis before electrolysis shows a more even topography of the electrode surface as shown in Fig. 1c. Whereas, the surface structure of the electrode after the 8 h of electrolysis depicts more deformed surface with visible deep and extended valley (dark spots in Fig. 1f). The depth of undulations was noted to be $\pm 1.5 \mu\text{m}$ and $\pm 4 \mu\text{m}$ on the electrode surface before and after the electrolysis, respectively.

3.2. Elemental characterization

The EDX elemental microanalysis was conducted to determine the bulk composition of metal oxide thin films on $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ electrode. The EDX elemental mappings on the surface of $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ electrode under the current density of 9 mA cm^{-2} , before and after the 8 h of electrolysis, are as shown in Fig. 2a–c and d–f, respectively. The atomic molar percentages of the precursor metals from EDX were found to be Sn- 91.7 at.% and Ta-8.3 at.% before and Sn-91.5 at.% and Ta-8.5 at.% after the electrolysis. The elemental composition of metals showed

reasonable agreement with the nominal mixture used [26]. Moreover, the atomic ratio of Sn/Ta from EDX (10.9) was more closed to the nominal ratio (12.33). This suggests that the Ti substrate is covered more uniformly with Sn, whereas Ta deposition is more dispersed. Overall, the metal fractions did not change noticeably before and after the electrolysis, though morphological changes existed.

3.3. Electrochemical characterization

The electrocatalytic activity of any electrode depends mostly on factors such as relative roughness factor of the electrode surface and the voltammetric currents associated with the degree of electroactive sites [27]. For the roughness factor, the current values for different sweep rates were measured at $E = 0.7 \text{ V}$ (vs. SCE), where an approximate symmetry for anodic and cathodic currents was recorded as shown in Fig. 3a. By plotting the anodic currents with respect to the scanning rates, a regression equation is deduced (shown in Fig. 3a, inset) as,

$$I (\text{A}) = 0.0001 v (\text{Vs}^{-1}) + 2.6 \times 10^{-6}, R^2 = 0.9977 \quad (6)$$

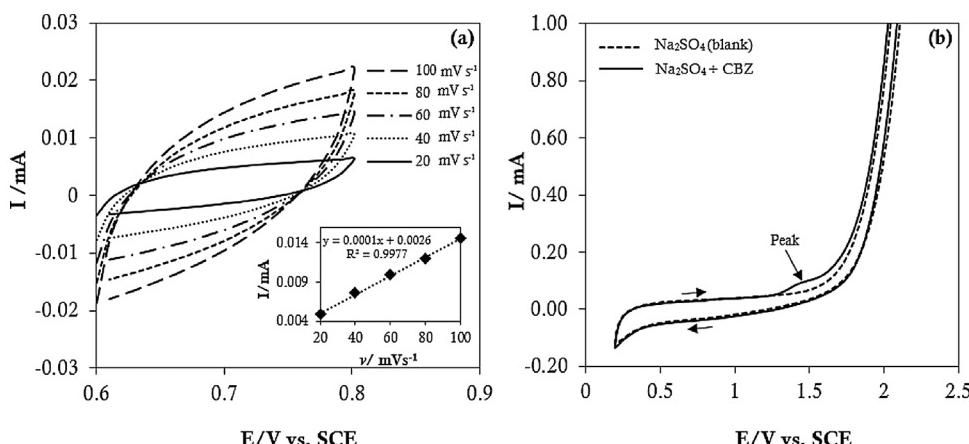
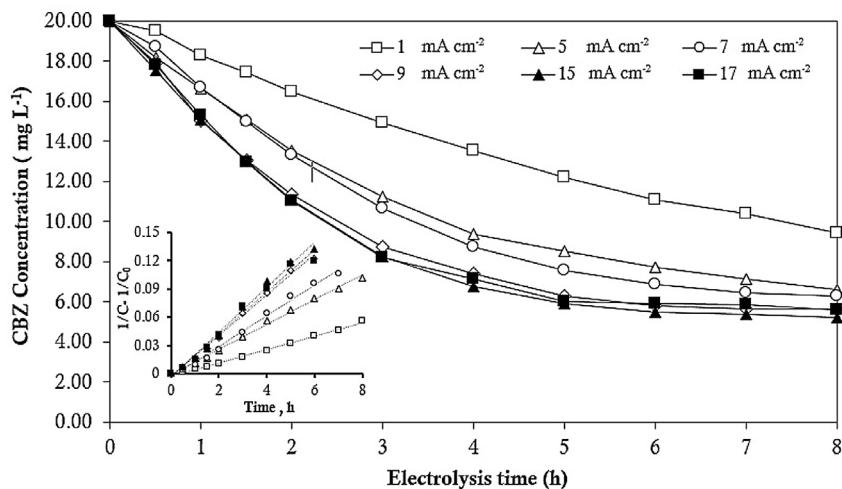


Fig. 3. Cyclic voltammograms of $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ in (a) double-layer region ($0.6\text{--}0.8 \text{ V}$) at scan rates from 20 to 100 mV s^{-1} in $0.1 \text{ M } \text{Na}_2\text{SO}_4$ solution. Inset: Linear regression of I versus v measured at $E = 0.7 \text{ V}$; (b) CBZ (30 mg L^{-1} , pH 5.7) with supporting electrolyte $0.1 \text{ M } \text{Na}_2\text{SO}_4$, scanned between $0.2\text{--}2.5 \text{ V}$ at scan rate of 100 mV s^{-1} .



The linear relationship between electric current and sweep rate shows that the Faradic current in this region is negligible, thus only the electric double-layer current is measured [27]. The double-layer charging current is much related to the double-layer capacitance of the electrode/solution interface as conductive layer was made of metal oxides [28]. So, the normalized capacitance of 0.0001 F cm^{-2} was calculated by dividing the slope value of Eq. (6) with the geometric surface area of the electrode. Further, the capacitance of the electrode surface was compared with that of a smooth surface oxide layer, with the capacitance of $8 \mu\text{F cm}^{-2}$ [27], which gave a relative roughness factor of 12.5. Therefore, the roughness of electrode surface has slightly improved by Ta doping over SnO_2 layer, which in turn have attributed a good electrocatalytic activity to the $\text{Ti/Ta}_2\text{O}_5\text{-SnO}_2$ electrodes. However, roughness factors of metal oxide films might vary by factor of several thousands with high discrepancy in magnitude between them [28].

Furthermore, CV tests were again performed to investigate the electrochemical property of CBZ molecule at $\text{Ti/Ta}_2\text{O}_5\text{-SnO}_2$ electrode, as shown in Fig. 3b. The oxygen evolution reactions (OERs) appeared between 1.7 and 2 V (vs. SCE) in both the solutions. In the presence of CBZ, a small anodic current peak was noticed at potential of 1.45 V (vs. SCE) in the voltammogram (Fig. 3b). The absent of more distinct peaks for CBZ oxidation might probably be due to the CBZ oxidation at a potential close to OER region. Furthermore, it can be noticed that there was no reduction peak recorded in the voltammogram during reverse scanning, which might be due to the irreversible characteristics of CBZ [29].

3.4. Effects of operating parameters on the removal of CBZ

3.4.1. Effect of current density

In electrochemistry, applied current density is the most important parameter which controls electron transfer and the generation of reactive oxidants [30], thus directly influences the removal rates of pollutants. Such major influencing role of current densities during the electrochemical removal of CBZ has been reported in many studies [5,6,20,23,31]. In this study, different current densities ranging from 1 to 17 mA cm^{-2} were applied in order to select an optimum current density with higher rate of CBZ removal as shown in Fig. 4.

It was observed that after the 8 h of electrolysis, the CBZ removal reached 53.0%, 67.0%, 68.5%, and 71.7% with corresponding current densities of 1, 5, 7, and 9 mA cm^{-2} , respectively. This trend is in accordance with the fact that increasing current density increases the organic pollution removal efficiency by the generation of more reactive oxygen species (*esp.* $\cdot\text{OH}$ radicals) [3,7,23]. The generated powerful $\cdot\text{OH}$ radicals then attack CBZ molecules and destruct it. Likewise, the CBZ removal rates were 73.8% and 72% at current densities of 15 and

Fig. 4. Effect of applied current densities on the removal of CBZ during electrolysis (CBZ₍₀₎: 20 mg L^{-1} + $0.1 \text{ M Na}_2\text{SO}_4$; pH 5.7; $T = 11 \pm 1^\circ\text{C}$) on $\text{Ti/Ta}_2\text{O}_5\text{-SnO}_2$ anodes. Inset: fitting of the different current densities to a pseudo-second order kinetic model.

17 mA cm^{-2} , respectively. Thus, beyond current density of 9 mA cm^{-2} , neither removal rate nor the kinetics increased noticeably. Two possible reasons might have associated with this phenomenon. First, the undesirable parasitic reactions of $\cdot\text{OH}$ radicals to O_2 gas or dimerization to weak oxidants such as $\cdot\text{OH}_2$ radicals, which could compete the main oxidation reaction (via $\cdot\text{OH}$ radicals), and can reduce the oxidation efficiency of the targeted pollutants [6,14,23,32]. Second, as anodic oxidation takes place heterogeneously with physio-adsorbed $\cdot\text{OH}$ radicals at electrode surface, electrochemical degradation rate after reaching the limiting current density might be directly proportional to the mass transfer rate of pollutants towards the electrode surface [23]. The current density of 9 mA cm^{-2} was selected as optimum current density for further study to ensure both an improved removal efficiency and a low energy consumption.

Furthermore, in order to evaluate the degradation kinetics of CBZ, the kinetic data were analyzed by using different kinetic models: pseudo-first order kinetic model and pseudo-second order kinetic model. The following Eqs. (7) and (8) were used for the pseudo-first order and pseudo-second order kinetic models,

$$\ln \frac{C_0}{C_t} = k_1 t \quad (7)$$

$$\frac{1}{C_t} - \frac{1}{C_0} = k_2 t \quad (8)$$

where C_0 is the initial concentration of CBZ; C_t is the concentration of CBZ at time t ; k_1 is the pseudo-first order rate constant (s^{-1}); and k_2 is the pseudo-second order rate constant ($\text{L mol}^{-1} \text{s}^{-1}$). The regression coefficients (R^2) for both pseudo-first order and pseudo-second order kinetics were compared corresponding to the different current densities as indicated in Table 1. The calculated values of R^2 from the pseudo-first order kinetic model were slightly lower than the value obtained from the pseudo-second order kinetic model. These results indicated that the pseudo-second order model better describes the degradation of CBZ by EO process. This is in

Table 1
CBZ removal efficiency (%), regression coefficient (R^2), pseudo-rate constant (k_{pseudo}), and half-life, as a function of current densities.

| Current densities (mA cm^{-2}) | 1 | 5 | 7 | 9 | 15 | 17 |
|---|-------|-------|-------|-------|-------|-------|
| % CBZ removal | 53.0 | 67.0 | 68.5 | 71.7 | 73.9 | 72.1 |
| Pseudo-First order model, R^2 | 0.998 | 0.971 | 0.980 | 0.971 | 0.970 | 0.950 |
| Pseudo-Second order model, R^2 | 0.997 | 0.996 | 0.993 | 0.995 | 0.991 | 0.983 |
| k_2 ($\text{L mol}^{-1} \text{s}^{-1}$) | 0.47 | 0.91 | 1.12 | 1.42 | 1.57 | 1.46 |
| Half-life (h) | 6.9 | 3.6 | 2.9 | 2.3 | 2.1 | 2.3 |

agreement with the previous work by J. D. García-Espinoza et al. [6], who also reported that the second-order was the best model to fit the kinetics in the electrochemical removal of CBZ with Ti/PbO₂ anodes. However, the pseudo-first order kinetic model for CBZ removal using an EO process have also been reported in other works [5,34,35]. In the present work, since R² values for both the models are comparable, the pseudo-first order model is also valid to describe the reaction kinetics of CBZ degradation. In this regard, it is worth noting that within 8 h of the reaction time, the formation of intermediate compounds could slightly distort the kinetic analysis.

The tendency of the enhanced CBZ removal efficiencies corresponding to the increased current densities are further supported with the results of pseudo-second order rate constant values, k_2 (Table 1). The increasing trend in the values of k_2 as a function of applied current densities indicates that amplified OERs are associated with increased current densities. With the increasing O₂ gas evolution, the mass transport phenomena increases indicatively leading to the enhanced diffusion flux of CBZ molecules towards anode surface, which subsequently increases k values [20]. From Table 1, at optimum current density of 9 mA cm⁻², the value of k_2 was 1.42 L mol⁻¹ s⁻¹ and the half-life was found to be 2.3 h. It indicates that 50% of the CBZ removal was reached within 2.3 h of electrolysis under the current density of 9 mA cm⁻².

3.4.2. Effect of initial CBZ concentration

It is obvious that the concentrations of CBZ fluctuates periodically or seasonally at wastewater treatment plants [89,36]. Therefore, it is more significant to investigate the effect of the initial concentration of CBZ on the removal efficiency of electrochemical treatment process. In this context, different concentrations of CBZ ranging from 2 to 30 mg L⁻¹ were electrolyzed under the constant current density of 9 mA cm⁻² for 8 h, in order to evaluate the influence of initial concentrations of CBZ on the removal efficiency, as shown in Fig. 5.

The removal rates of about 80.3%, 73.3%, 71.8%, and 70.2% were achieved after the 8 h of electrolysis when initial concentrations of CBZ were 2, 10, 20, and 30 mg L⁻¹ respectively (Fig. 5, inset). The removal rate was much faster during the first 2 h of operation in all of the four different assays, however, decreased from 80.3 to 70.2%, when the initial CBZ concentrations increased from 2 to 30 mg L⁻¹. About 70% of CBZ removal was achieved within 3.5 h of electrolysis for 2 mg L⁻¹ of initial CBZ concentration, whereas 8 h were needed to achieve the same CBZ removal for initial CBZ concentration of 30 mg L⁻¹. These results are consistent with other works in which electrochemical degradation gave better results at low initial concentration [21,23,31].

At higher initial concentrations, the mass transfer of organic substances increases, which ultimately inhibits the interaction between the targeted pollutant and anode active sites [21,23]. This can generate

more intermediate products, which in turn competes with CBZ in the reaction with ·OH radicals and can reduce the CBZ removal efficiency [21]. So, while increasing the initial concentration of CBZ under identical current densities, the oxidation process can be limited by the formation of ·OH radicals [20]. Further, the electrode surface might be mediated with passivation (diffusion layer) due to the deposition of more reaction products. On the other hand, at lower concentrations, the higher CBZ removal rate was achieved, which indicates that the greater amount of CBZ molecules are attacked by the ·OH radicals. This result can be explained by the phenomena that at low initial concentrations, electrochemical degradation rates of organic molecules can be faster than the diffusion of side-products [21].

3.4.3. Effect of pH

pH values can have a significant influence on the electrochemical treatment processes [19]. To assess the effect of pH on the removal efficiency of CBZ at Ti/Ta₂O₅-SnO₂ anode, different initial pH conditions ranging from acidic to basic media (2–10) were investigated. Fig. 6 depicts the degradation kinetics of CBZ (20 mg L⁻¹) when electrolyzed for 8 h under the current density of 9 mA cm⁻² with supporting electrolyte of 0.1 M Na₂SO₄. In Fig. 6 (inset), the residual concentrations of CBZ after the 8 h electrolysis are found to be decreasing from about 6.3, 5.7, and 5.0 mg L⁻¹ at initial pH values of 2, 4, and 6, respectively. However, the residual concentrations are in increasing trend in basic media ranging from 5.7 to 6.0 mg L⁻¹ at corresponding pH values of 8 and 10, respectively. Under the identical conditions, the optimum removal of 75.2% was achieved at pH value of 6. Whereas, the removal efficiencies were 68.8%, 71.2%, 71.5%, and 70.1% at the pH values of 2, 4, 8, and 10, respectively. Thus, these results indicate that the influence of pH was not significant for electrochemical removal of CBZ, which is in agreement with other studies [3,6,23]. The reason might be the high acid-dissociation constant (pK_a) of CBZ (13.94), for which no significant dissociation is generally reported, either in acidic or basic conditions [6]. In practice, this tendency will be useful in real treatment cases since MBR processes are normally operated at pH of 6–7 [9]. On the other hand, the decreasing trend of the CBZ removal efficiency with increasing pH values might be attributed to the significant shift of OER onset potential to less positive values (low O₂-overvoltage), which favors more oxygen formation than pollutant oxidation [37]. It was also noticed that the solution pH did not change significantly in acidic assays over the 8 h of time. Nevertheless, the solution pH was found to be changing into a more acidic character (5–6) when performed in alkaline media (pH 8–10 initially), which might be due to the formation of weak acid products such as carboxylic acids [32,38].

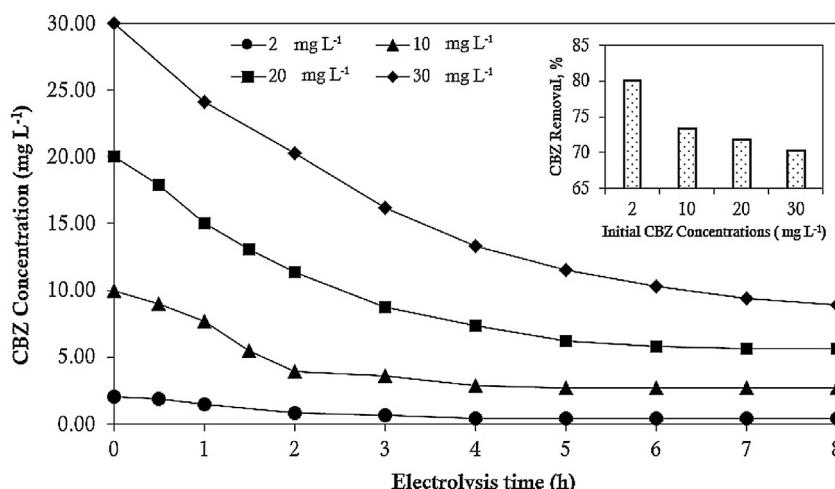


Fig. 5. Effect of the initial CBZ concentrations on the removal tendency during electrolysis (CBZ₍₀₎: 1–30 mg L⁻¹; 0.1 M Na₂SO₄; pH: 5.7; T = 11 ± 1 °C; current density: 9 mA cm⁻²) on Ti/Ta₂O₅-SnO₂ anodes. Inset: CBZ removal efficiencies at different initial CBZ concentrations (2, 10, 20, and 30 mg L⁻¹).

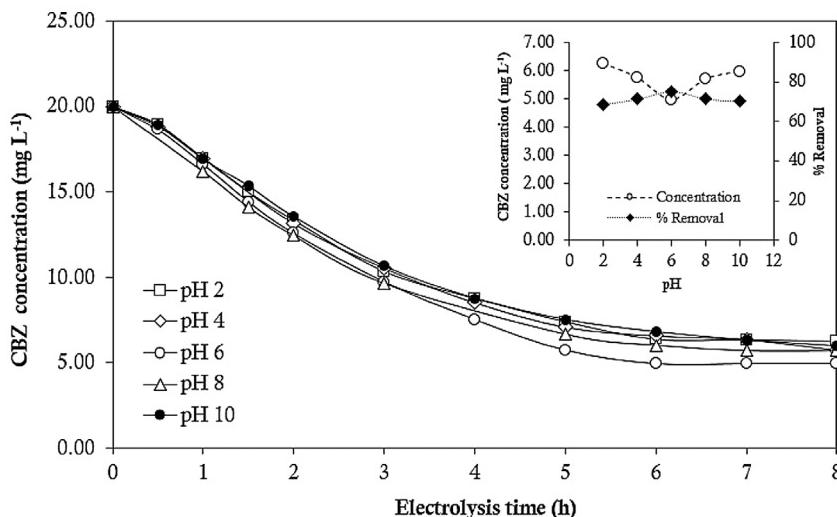


Fig. 6. Effect of initial pH on the removal tendency of CBZ during electrolysis (CBZ $_{(0)}$: 20 mg L^{-1} + $0.1 \text{ M Na}_2\text{SO}_4$; current density: 9 mA cm^{-2} , $T = 11 \pm 1^\circ\text{C}$) on $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ anodes. Inset: Residual concentrations and corresponding CBZ removal% after 8 h of electrolysis at different pH.

3.4.4. Effect of temperature

The reaction rate constants are exponentially dependent on the temperature of the medium following the Arrhenius law. The similar principle can be expected in the electrochemical processes. Therefore, to investigate the effect of temperature on the electro-oxidation, 20 mg L^{-1} of CBZ solution was electrolyzed on $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ anode under the current density of 9 mA cm^{-2} at three different temperatures ranging from 10 to 30°C . Fig. 7 shows the effect of different temperatures on the CBZ degradation kinetics during 8 h of electrolysis. The removal efficiencies of 71.7% , 74.1% , and 75.5% were achieved when corresponding operating temperatures were maintained at 10°C , 20°C , and 30°C (Fig. 7, inset). Thus, increasing the temperature had a slight positive influence on the kinetic rates. One possible reason might be a better mass transfer of pollutants towards the anode surface at higher temperature, due to high molecular agitation which could enhance the oxidation efficiency [39]. Another reason might be the indirect oxidation reaction of organics in the bulk solution by electrogenerated oxidants peroxodisulphates ($\text{S}_2\text{O}_8^{2-}$), which is one of the powerful oxidizing species, from the oxidation of electrolyte (Na_2SO_4). Indeed, it was reported that the rate of oxidation of organic pollutants via peroxodisulphates increases with positive increments in the solution temperature [31]. In terms of hydrodynamics of the bulk solution, viscosity decreases with increasing solution temperature, which enhances mass transfer rate of organic species towards electrode surface thus contributes higher oxidation efficiency [20].

Moreover, the degree of mineralization was also analyzed at this stage under the optimum operating conditions. Using current density of 9 mA cm^{-2} , pH of 6.0 and initial CBZ concentration of 20 mg L^{-1} , optimum removal of TOC were 61.2% , 69.8% and 71.1% under the solution temperatures of 10°C , 20°C , and 30°C , respectively (Fig. 7, inset). Therefore, the average rate of mineralization during this work was about 61% , as the operating temperature was maintained at about $11 \pm 1^\circ\text{C}$. It can be concluded that increase in the temperature has positive effect on the degree of mineralization too. Nevertheless, the mineralization efficiency was always lower than that of CBZ (71.1% and 75.5% , respectively). The most possible reason might be attributed to the fact that carboxylic acids are highly recalcitrant, thus they degrade slower than parent compounds [32].

3.5. Comparison between $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ and Ti/PbO_2 electrodes

In order to evaluate the effect of different electrode materials on the CBZ removal efficiencies, $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ and Ti/PbO_2 electrodes were compared. The stability of both electrodes were also compared by performing leaching tests. Fig. 8 shows the removal kinetics of 20 mg L^{-1} CBZ in aqueous $0.1 \text{ M Na}_2\text{SO}_4$ solution, pH 6.0 , $T = 10^\circ\text{C}$, and using current density of 9 mA cm^{-2} . The removal trends of both $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ and Ti/PbO_2 electrodes were almost identical until 2 h of electrolysis. However, after 8 h of electrolysis, the CBZ removal efficiency reached 71.7% and 77.9% on $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ and Ti/PbO_2

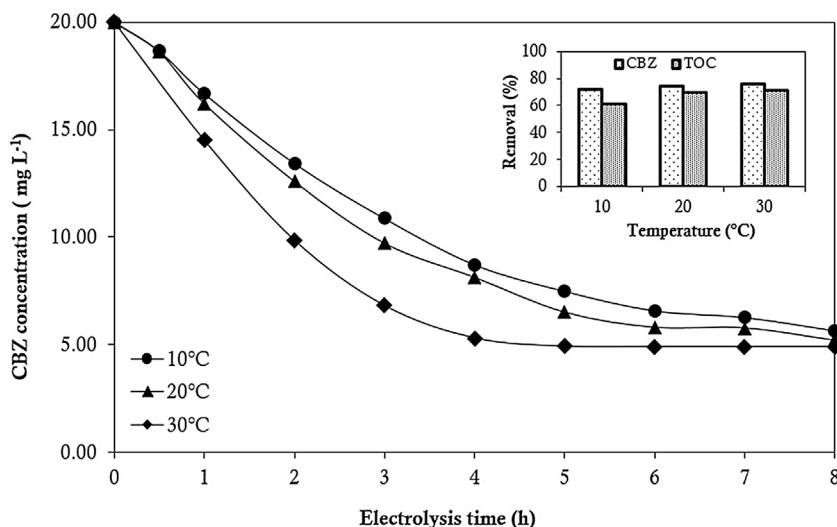


Fig. 7. Effect of temperature on the removal tendency of CBZ during electrolysis (CBZ $_{(0)}$: 20 mg L^{-1} + $0.1 \text{ M Na}_2\text{SO}_4$; current density: 9 mA cm^{-2} ; pH: 6) on $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ anodes. Inset shows% removal of CBZ and TOC at different temperatures.

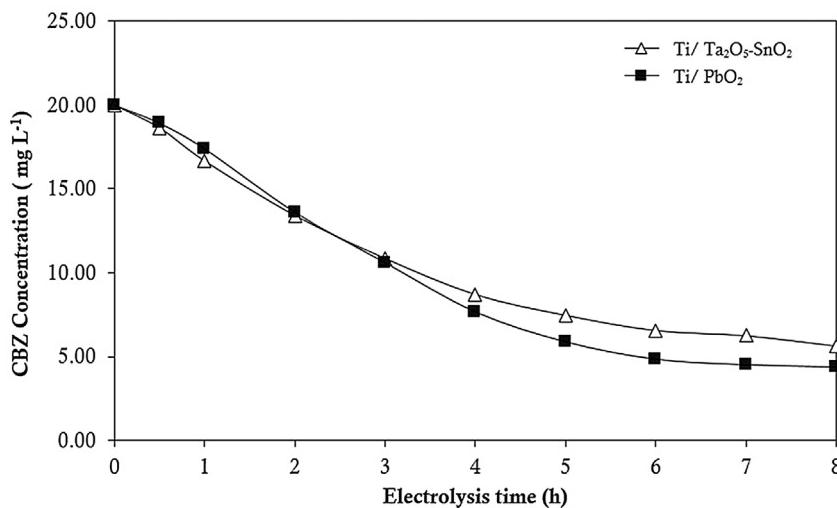


Fig. 8. The comparison on the removal tendencies of CBZ during electro-oxidation (CBZ₍₀₎: 20 mg L⁻¹ + 0.1 M Na₂SO₄; current density: 9 mA cm⁻²; pH: 6, T = 10 °C) on Ti/Ta₂O₅-SnO₂ and Ti/PbO₂ anodes.

anodes, respectively (Fig. 8). From the results, it can be concluded that under the identical operating conditions, the Ti/PbO₂ electrode is more effective on CBZ removal. This tendency could be explained by the fact that the Ti/PbO₂ anodes have greater electrocatalytic activity than Ti/Ta₂O₅-SnO₂ anodes due to their higher relative roughness factor [40]. The increase in surface roughness can produce larger amount of physisorbed ·OH radicals under the identical current density [21], which could react rapidly with all organic species at the vicinity of anode surface [31].

Furthermore, stability of both the electrodes was examined in terms of the leaching of Ta, Sn, Ti and Pb, by monitoring their ion concentrations in the bulk solution. Each electrodes were electrolyzed for 24 h by reusing the same electrodes over three days (8 h per day with fresh solutions each run), as mentioned in Fig. 9a,b.

In Fig. 9a, the dissolution profile of Ti/PbO₂ anode exhibits no leaching of Pb during the first 8 h of electrolysis. However, the dissolution of PbO₂ was significant to bulk solution during 16 h and 24 h of the electrolysis, releasing higher amounts of Pb (concentrations of 37.3 and 25.8 µg L⁻¹, respectively). Likewise, traces of Ti ions were also measured from the solution with maximum of 14.2 µg L⁻¹ during the first 8 h of electrolysis. These results show that current density of 9 mA cm⁻² is capable of dissolving PbO₂ from the electrode surface. A significant concentration of Pb leached from PbO₂ oxide coated electrodes has also been reported in another work [20]. It is worth noting that the maximum allowable concentration of Pb in surface water resources, according to EU directive is 14 µg L⁻¹ [41].

On the other hand, leaching profile of Ti/Ta₂O₅-SnO₂ shows the increasing trend for Sn and Ti, as compared to Ta (Fig. 9b). The leaching of Sn was the highest with concentrations of 145.7, 318.2, and 407.3 µg L⁻¹, respectively after 8, 16 and 24 h of electrolysis. Similarly, Ti concentration increased from 53.6 to 92.9 µg L⁻¹ after 8 and 24 h of

electrolysis, respectively. In contrast, the leaching of Ta was measured only in the range of 2–14 µg L⁻¹, indicating a low dissolution in to the bulk solution. In this regard, currently there are no specific regulations on the concentrations of Ti, Sn, or Ta in surface water sources. Moreover, the CBZ removal efficiency of Ti/PbO₂ and Ti/Ta₂O₅-SnO₂ was comparable, nonetheless the latter is more environmentally friendly since the leaching phenomenon (frequently associated with EO) will not generate heavy metals into the treated waters.

3.6. The energy consumption

The electrical energy consumed to treat specific volumes polluted solutions is the prime concern to assess the viability of any electrochemical degradation processes. The EC evolved during the electrochemical degradation of CBZ at varying current densities (Cf. Section 3.4.1) are shown in Fig. 10. It indicates that the minimum electrical energy consumption of 3.2 kWh m⁻³ was required to reach 53% of CBZ removal while using the current density of 1 mA cm⁻². The EC increased from 26.3 to 60.3 kWh m⁻³ when current densities increased from 5 to 9 mA cm⁻². Beyond the current density of 9 mA cm⁻² until 17 mA cm⁻², the EC increased from 60.3 kWh m⁻³ and reached to 172.7 kWh m⁻³, even though the removal efficiencies were not improved significantly. For the optimum current density of 9 mA cm⁻², the energy required to degrade 71.7% of CBZ was 60.3 kWh m⁻³. It has been observed that the current densities higher than the limiting one (9 mA cm⁻² in the present study) can be associated with high energy consumption. The reason can be that a large mass of OH radicals might be evolved to O₂ due to parasitic reactions, then a large cell voltage is often used mostly for O₂ generation, which does not help further in oxidizing the organic pollutant [31].

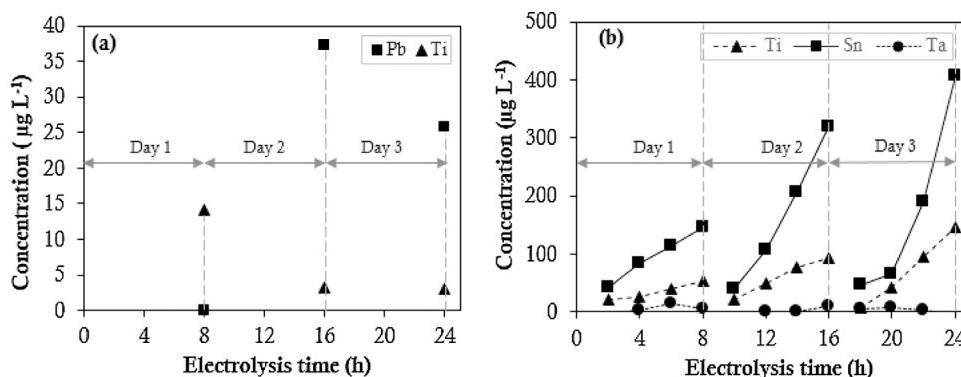


Fig. 9. Leaching profile of Pb, Ta, Sn, and Ti from (a) Ti/PbO₂ and (b) Ti/Ta₂O₅-SnO₂ anodes when electrolyzed for 24 h by reusing the same electrodes but using fresh working solutions (CBZ₍₀₎: 20 mg L⁻¹ + 0.1 M Na₂SO₄) for each assays; under current density of 9 mA cm⁻².

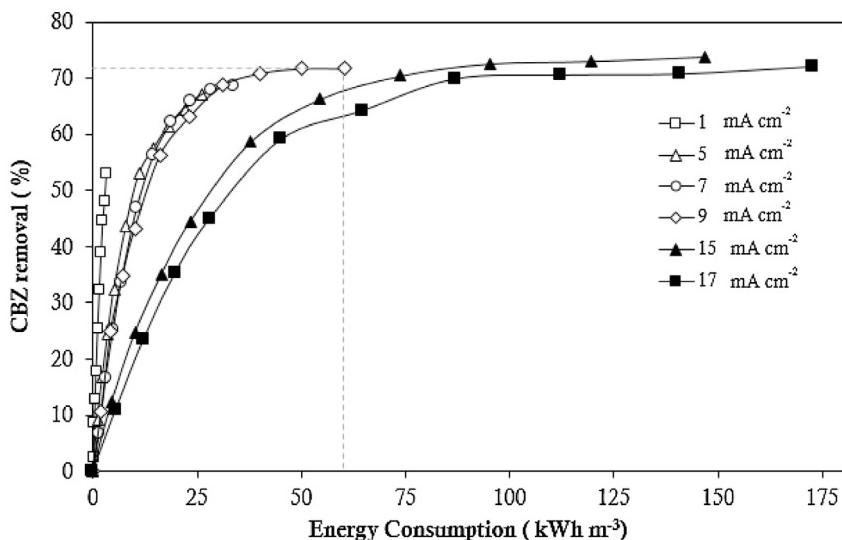


Fig. 10. The electrical energy consumption trend against the CBZ removal efficiency during the electrochemical oxidation (CBZ₍₀₎: 20 mg L⁻¹; 0.1 M Na₂SO₄; pH: 5.7; T = 11 ± 1 °C) on Ti/Ta₂O₅-SnO₂ anode under different current densities.

3.7. Applicability of EO process in real MBR effluent for CBZ removal

In practice, the optimum operating conditions during the removal of CBZ from synthetic solution were applied for the treatment of CBZ in the real MBR effluents, collected from a local MBR pilot. The characteristics of the MBR effluent, detailed specifications and operating conditions of the MBR pilot plant are described in previous study [9]. The MBR effluent samples were then spiked with a precise amount of CBZ to have an initial concentration of 10 µg L⁻¹. Moreover, two different working solutions, with or without supporting electrolyte, were prepared and experimented. The details of experimental conditions and results are presented in Table 2.

From Table 2, it can be noticed that the EO method, which was operated under optimal conditions, has shown an excellent CBZ removal efficiencies in the real MBR permeate, independent of the influence of supporting electrolyte. About 90% removal of CBZ was attained after 2 h of electrolysis, which further reached 99.99% within 4 h of electrolysis, for both assays (data not shown). These results are consistent with the findings of García-Gómez et al. [2], where low concentrations of CBZ spiked into the synthetic wastewater was electrolyzed by using EO method. Nevertheless, the energy consumption was higher when no supporting electrolyte was used as compared to the use of it (Table 2). High salinity of effluent wastewater could increase the conductivity and thus can lower the energy consumption [1]. Nonetheless, the conductivity of the MBR effluent in this work was reported to be 601 µS cm⁻¹, which was not enough to maintain a constant electrical pressure during the redox reactions. On the other aspect, the cost of using supporting electrolyte (approx. US\$ 70 per metric ton) is much cheaper than the consumption of electricity (approx. US\$ 0.05 per kWh).

4. Conclusion

The electrochemical oxidation of CBZ from synthetic solutions and

real MBR effluents using a newly developed Ti/Ta₂O₅-SnO₂ electrodes was investigated under galvanostatic conditions. The characterization of the Ti/Ta₂O₅-SnO₂ electrodes were performed by using SEM, EDX, AFM, and cyclic voltammetry analyses. The main operating parameters influencing the CBZ removal efficiency in synthetic solutions on the tested anodes were evaluated as a function of applied current density, initial CBZ concentration, pH, and temperature. The results showed that the maximum removal of CBZ (20 mg L⁻¹) and TOC reached 75.5%, and 71.1%, respectively, after 8 h of electrolysis, current density of 9 mA cm⁻², solution pH 6, temperature of 30 °C, and using 0.1 M Na₂SO₄ as supporting electrolyte. The performance of Ti/Ta₂O₅-SnO₂ electrode was compared with Ti/PbO₂ electrode in terms of CBZ removal efficiencies and stability. The results showed that, under the same conditions, the CBZ removal efficiency of Ti/PbO₂ electrode was slightly higher when compared with the investigated electrode, but the latter was more environmentally friendly. Besides, achieving an optimal CBZ removal efficiency of 71.7% required the lowest energy consumption of 60.3 kWh m⁻³.

Furthermore, the complete degradative removal of CBZ was achieved in spiked real MBR effluents, under the optimal operating conditions. Overall, the EO based on the use of novel Ti/Ta₂O₅-SnO₂ electrode was found to be a reliable process to remove CBZ from contaminated waters, with promising potential for integration with MBR technology to remediate CBZ.

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Table 2

Electrochemical oxidation experiments on real MBR effluent for the validation of CBZ removal (Current density: 9 mA cm⁻²; pH: 6; T: 11 ± 1 °C; at Ti/Ta₂O₅-SnO₂ anodes).

| Parameter | Initial concentration in MBR effluent | Final concentration after 8 h of electrolysis | Electrolyte | Removal (%) | EC (kWh m ⁻³) |
|---------------------------|---------------------------------------|---|---|-------------|---------------------------|
| CBZ (µg L ⁻¹) | 10.75 ± 0.35 | < 0.07 (LOD) ^a | No electrolyte 0.1 M Na ₂ SO ₄ | 99.99 | 109.4 |
| | | < 0.07 (LOD) ^a | | 99.99 | 57.2 |

^a (LOD) Limit of detection.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.09.017>.

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